Study of Interfacial Chemistry between Metals and Their Effects on Electronic Systems

Sponsored by
Defense Advanced Research Projects Agency (DOD)
and
The Office of Naval Research (ONR)

ARPA Order No. 3564 Amd 8
Contract No. N00014-83-K-0073: Modification P00006
DARPA Order 5674
NR 4147126-02

Semiannual Technical Report: April 1, to September 30, 1986
Effective date of contract: 10-1-85
Contract dates: 10-1-85 to 9-30-88

Principal Investigators: W. E. Spicer and I. Lindau
Stanford Electronics Laboratories
Stanford University
Stanford, CA 94305
(415) 723-4643

Electrical Study of Schottky Barrier Heights on Atomically Clean p-type InP (110) Surfaces

We studied the electrical properties of a large number of metal (Ag, Cr, Cu, Au, Pd, Mn, Al, Ni)/p-type InP diodes which were fabricated by *in situ* metal deposition on atomically clean InP (110) surfaces in ultra high vacuum. Schottky barrier heights were determined from current-voltage (I-V) and capacitance-voltage (C-V) measurements. We found a small, but significant range in barrier heights (0.76 eV to 0.98 eV). Comparison of these p-type results to our earlier work on n-type surfaces shows that for these interfaces, the Fermi level of *n*-type and *p*-type samples is pinned at the same energy within the bandgap. (These results are similar to those previously reported by us for the GaAs interfaces prepared under the same conditions (only the absolute values of the pinning energies are different). Our results indicate that Schottky barrier models that use metal-independent interface states and potential normalization conditions (i.e. natural band lineups) can predict the general trends in the interface Fermi level pinning behavior. They fail, however, to provide quantitative agreement with experiment. We applied a theoretical method to determine the natural band lineups at the interface (using a scheme due to O.K. Anderson) and found that the use of work functions or electronegativities gives analogous correlations. Also investigated was the effect of air exposure on the electrical characteristics of diodes. For *in situ* I-V measurements, the metal/semiconductor systems were characterized by a near unity (1.03-1.10) ideality factor *n*. Upon exposure to air we found a large increase in the current and ideality factor *n* for several (Cu, Au, Pd, Mn, Ni) metal/*p*-type InP systems at all measured biases. A detailed investigation of the Pd/*p*-type InP system indicated that the "excess" current pathway which results from exposure to air is at the periphery and can be eliminated by mesa etching. A similar mechanism is most likely at play for other systems.

* This work was partially supported by the Air Force Contract.

Fermi level pinning for very thin metallic overlayers

We extended the studies of Schottky barrier formation (Fermi level pinning) to very low metal thicknesses. These studies of the initial stages of Schottky barrier formation are extremely important to elucidate mechanisms responsible for the rectifying barrier. A specially built evaporator allowed reproducible metal exposures as low 1/10000 of monolayer. We find that surface Fermi level movement is an exponential function of the coverage. These data cannot be explained by existing models of the Schottky barrier

formation. Several possible mechanisms for this behavior are currently being considered. At this time the most plausible explanation seems to be given by the microscopic cluster model developed by us in cooperation with S. Doniach. Computer modeling of the data using this approach is now in progress.

Amophous Si/InP heterojunction interface.

We studied the Si/InP interface [1] at coverages up to 12 ML. The interface is stable with respect to temperature up to 300°C, and grows with a uniform layer for the first several monolayers (morphology information is not available above 3 ML). The Fermi level is pinned by n-gap defect states induced by the silicon at 0.4 eV below the conduction band minimum at and above the first monolayer. The valence band discontinuity is 0.56 ± 0.1 eV and 0.46 ± 0.1 eV for the 20°C and 280°C substrate growth temperatures. The difference is within experimental error, and in agreement with experiments results in the literature [2].

The overlayer is not epitaxial and all apparent surface long range order (measured by Low Energy Electron Diffraction) disappears by one monolayer. Crystallites are not forming and the overlayer is amorphous Si. Current theories for the valence band discontinuity for this system are performed for an ideal, epitaxial (yet unstrained) interface and achieve only modest agreement with the experiment. Harrison's Universal Parameter Tight Binding Theory [3] predicts $\Delta E_V = 0.1$ eV and Tersoff's complex band structure alignment [4] theory gives 0.40 eV. More work needs to be done on epitaxial and non-epitaxial interfaces before all of the important physical effects are identified and included in the theories.

1. P. H. Mahowald, R. S. List, J. Woicik, P. Pianetta and W. E. Spicer, Phys. Rev. B 34, 7069 (1986).
2. A. D. Katnani, G. Margaritondo, Phys. Rev. B 28, 1944 (1983).
3. W. A. Harrison, Phys. Rev. B 24, 5835 (1981).
4. J. Tersoff, Phys. Rev. B 30, 4874 (1984).

Chemistry and Schottky barrier formation at the Ti and Pt/GaAs interfaces

New studies of Pt and Ti on GaAs were performed at SSRL using SXPS. The objective of the Pt experiments was to investigate the room temperature chemical reactions on n-type material and to confirm UPS studies on the surface Fermi level pinning on p-type material.

The Ti experiments concentrated on the effects of annealing on n-type GaAs. In addition, a room temperature experiment with Ti on p-type GaAs investigated whether or not atomic exchange reactions occur for this system. Analysis of the data from the Pt experiments showed very good agreement with the earlier UPS results. Extensive computer analysis using curvefitting routines to separate surface, substrate, and reacted components was used. The Fermi level stabilized at ~0.5 eV above the VBM on both n- and p-type GaAs. The overlayer/substrate intermixing was found to be similar to that observed for the Au-GaAs system. A Pt-Ga compound was found at an energy 0.4 eV lower in energy (with respect to Ga in GaAs), which is in good agreement with calculations performed by Nogami [1] to determine energy shifts for Ga in infinite dilution in an overlayer matrix. The As 3d spectra chemistry show evidence of two bonding configurations which appear at submonolayer coverages. As the overlayer develops one of the components dominates and stabilizes at an energy ~ 0.3 eV higher than the As in GaAs. We began analysis of the Ti annealing data. These results show greater outdiffusion of the substrate constituents than for Pt overlayers. There is an increase in the width of the Ti-Ga layer from that observed at room temperature with a corresponding increase in the Ti-As layer width. The elemental Ga appears to be trapped near the overlayer-semiconductor interface because at a coverage of 6.7 ML the binding energy of the Ga peak increases from the room temperatue value. Also, the Ti-As layer seems to inhibit further outdiffusion of the Ga. The stoichiometry Ti-As compound appears to be fairly stable with temperature, as there is little change in the energy of this peak.

1. J. Nogami, T. Kendelewicz, I. Lindau, and W. E. Spicer, Phys. Rev. B 34, 669 (1986).

Chemical reaction at the In on GaAs interface- a synchrotron radiation study.

We have recently reported a PES study of the chemical reaction at the In on GaAs interface, in which 40.8 eV photons from a Helium discharge lamp were utilized as the light source [1]. Upon annealing the interface above the In melting point, the In 4d spectrum contained a component shifted to 0.8 eV higher binding energy from the unreacted In 4d peak. This component is indicative of In bonded covalently, as in InAs. Consequently it was suspected that the energetically unfavorable replacement reaction c In + GaAs --> $In_xGa_{1-x}As$ + $In_{c-x}Ga_y$ + (x - y) Ga occurs at the interface. However, Ga 3d signals from the segregated elemental Ga and alloyed Ga reaction products could not be resolved. We suspected that the failure to resolve these signals was due to the proximity in binding energy of the elemental Ga 3d core level and the covalent In 4d core level. At 40.8 eV, the

photoionization cross section of In 4d is 7.5 times that of Ga 3d, and hence a potential elemental Ga 3d signal would be washed out by the stronger In 4d. Thus to study the possibility of a replacement reaction, synchrotron radiation, which allows adjustment in relative signal strength between the In 4d and Ga 3d peaks, was utilized. The In 4d cross section passes through a Cooper minimum, and as a result, at roughly 140 eV the Ga 3d to In 4d signal ratio is maximized. With the In 4d signal minimized, we can see that the Ga 3d spectra from the annealed surfaces have nearly the same width and lineshape as that of the clean surface. The photoemission spectra of the annealed In / n-GaAs (110) interface thus show no evidence of the elemental Ga reaction product expected for a replacement reaction. One possible explanation is that the elemental Ga was sufficiently alloyed in In or clustered to be difficult to detect with PES. It must be noted that in the case of Al on n-GaAs such a difficulty does not occur, and the segregated Ga peak is clear in the Ga 3d spectrum. Another possibility is that upon heat treatment the molten In reacts with excess As, which has been reported to exist in GaAs. We have not detected free As in our PES measurements. Certainly the existence of significant quantities of excess As in GaAs would have implications on reactions beyond the In / GaAs system under study, and whether the reactions observed in other GaAs systems are consistent with such an excess must be investigated.